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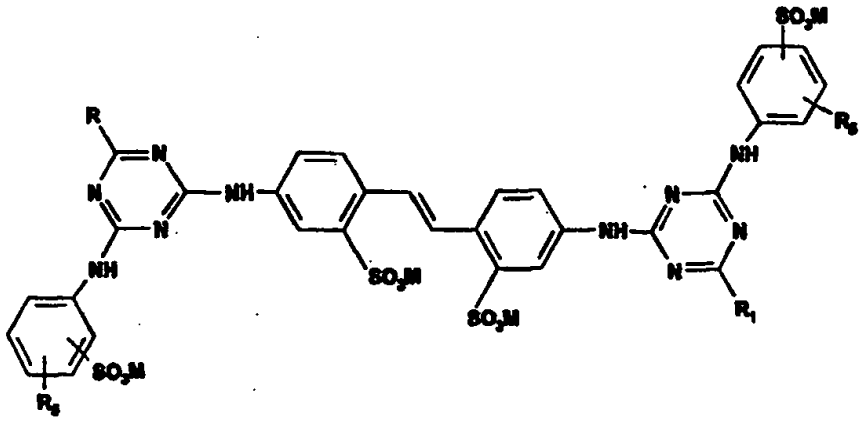
(54) Title: OPTICAL BRIGHTENING AGENTS



(I)

(57) Abstract

Optical brightening agents for use in textiles, paper, detergents correspond to formula (I) where R, R_1 are preferably derived from the amino acids, particularly glutamic and iminodiacetic acids.

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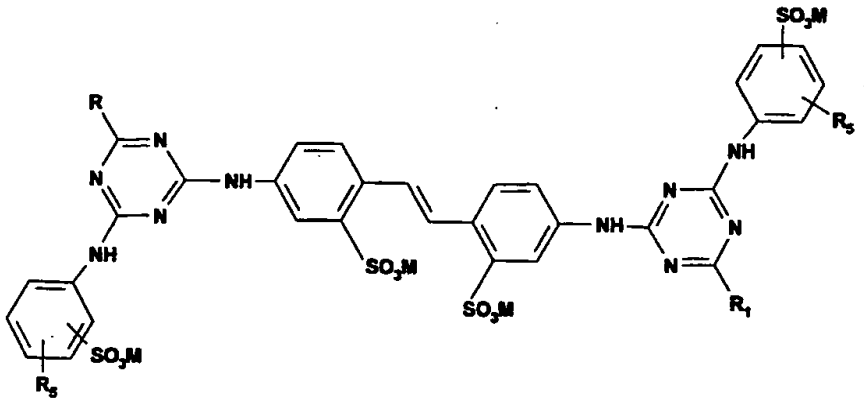
Optical Brightening Agents

This invention relates to novel organic compounds based on 4,4'-diaminostilbene-2,2'-disulphonic acid.

4,4'-diaminostilbene-2,2'-disulphonic acid., known generally as "DAS", is the starting material for a number of important products used in industry, most importantly various dyestuffs and optical brighteners. DAS-based optical brighteners (OBAs) find a wide range of uses in detergents, paper, textiles and so on.

One of the standard ways of making an optical brightener is to substitute the amino groups of DAS with substituted triazines. This may be done, for example, by reacting DAS with cyanuric chloride and then further reacting the remaining chlorines on the cyanuric chloride moiety. A popular substitutent for one of these chlorines is provided by sulphanilic acid.

It has now been found that it is possible to make a new class of DAS-based compounds whose performance is substantially better than that of known sulphanilic acid-based materials. The invention therefore provides a compound in free acid or salt form of the formula I



I

wherein

R, R_1 are moieties which are the same or different and have the formula $-NR_2R_3$, wherein: (a) R_2 is selected from

(i) hydrogen;

(ii) C_{1-6} alkyl, optionally substituted with at least one of mercapto, C_{1-6} thioalkyl, OH and SO_3M; and

(iii) $-R_4(CO_2M)_x$

wherein R_4 is an aliphatic moiety having from 1-6 carbon atoms, those valencies not bonded with groups CO_2M being bonded with at least one of H, mercapto, C_{1-6} thioalkyl, OH and SO_3M, x is an integer of from 1 - 4 and M is selected from hydrogen, a colourless cation or an amine-derived cation;

with the proviso that, when R_2 is selected only from (i) or (ii), any group (ii) is substituted with at least both of OH and SO_3M;

(b) R_3 is selected from groups R_2, hydrogen and C_{3-6} alkyl, with the provisos that R_2 and R_3 cannot both be hydrogen, and when one of R_2, R_3 is hydrogen, the other cannot be $-(NHCH_2CO_2H)$;

or R_2 and R_3 together with the nitrogen atom form a ring having from 5-6 members only one of which is heterocyclic, which ring is singly substituted with -COOM or $-SO_3M$; and R_5 are selected independently from the group consisting of hydrogen, methyl, C_{1-6}alkoxy and halogen.

In a preferred embodiment of the invention, R_5 is hydrogen and the sulphonic acid groups on the phenylene rings attached to the triazine rings are meta or para to the connecting amino groups, that is, the particular moieties attached to the triazine rings are derived from sulphanilic acid or metanilic acid.

The moieties R and R_1 may be derived from any suitable compounds known to the art. It is preferred that they be amino-acid residues. Examples of suitable acids include glycine, aspartic acid, serine, hydroxyglutamic acid and alanine, but the preferred acids are glutamic

acid and iminodiacetic acid.

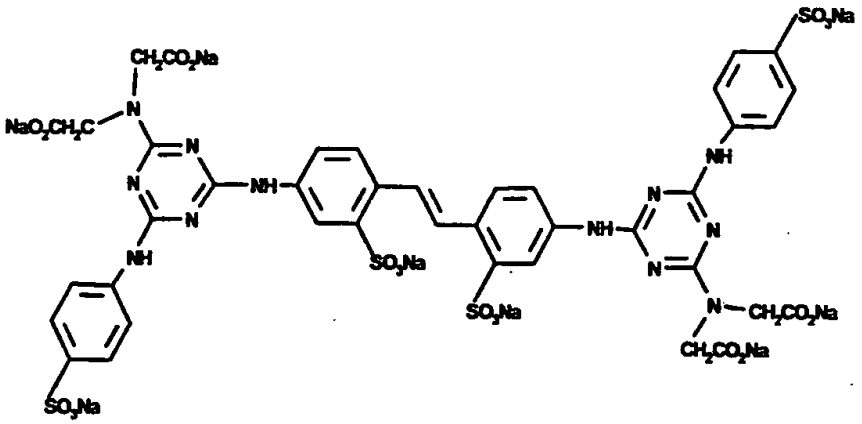
The most preferred compounds are those derived from metanilic acid or sulphanilic acid and where R is derived from glutamic or iminodiacetic acid.

In the case where R_2 and R_3 together with the nitrogen atom of groups R, R_1 form a ring, it is preferred that this ring be a pyrollidine ring substituted with -COOM.

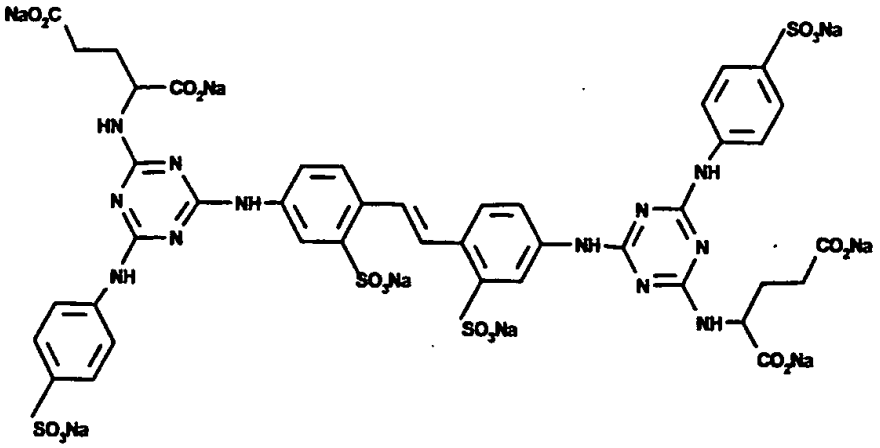
The compounds according to the invention may be prepared in free acid form or in salt form such as with an alkali metal cation, an organic amine salt, a mixed or partial salt.

The materials M are preferably either metal cations, particularly sodium and potassium, or simple alkanolamines such as mono-, di-and triethanolamine.

Two of the most preferred compounds have the formulae II and III

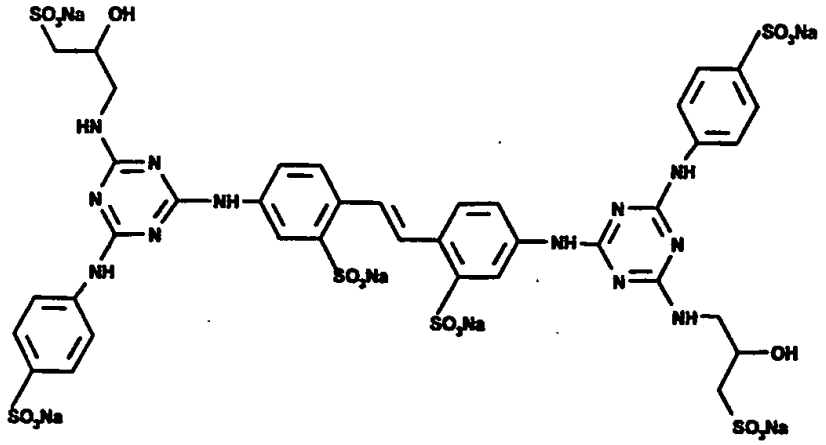


II

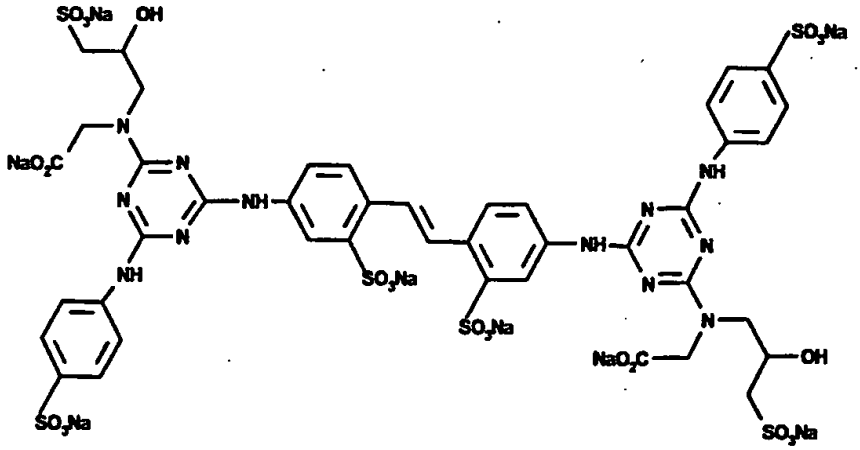


III

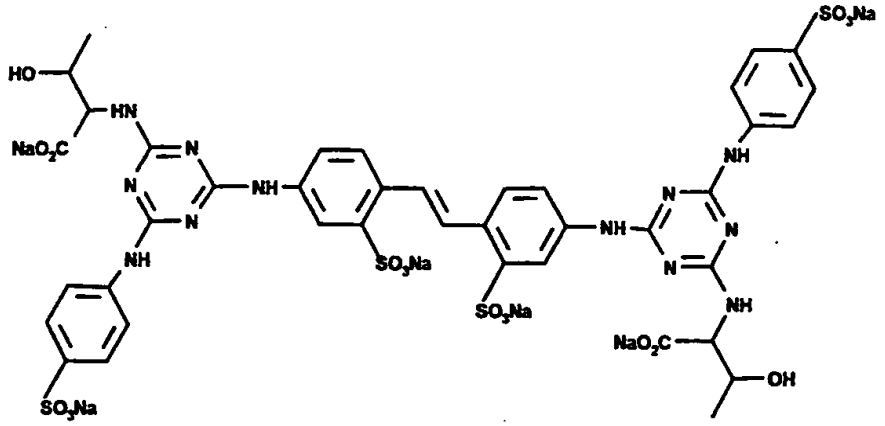
Other compounds which also perform well are those which have the formulae IV - XI



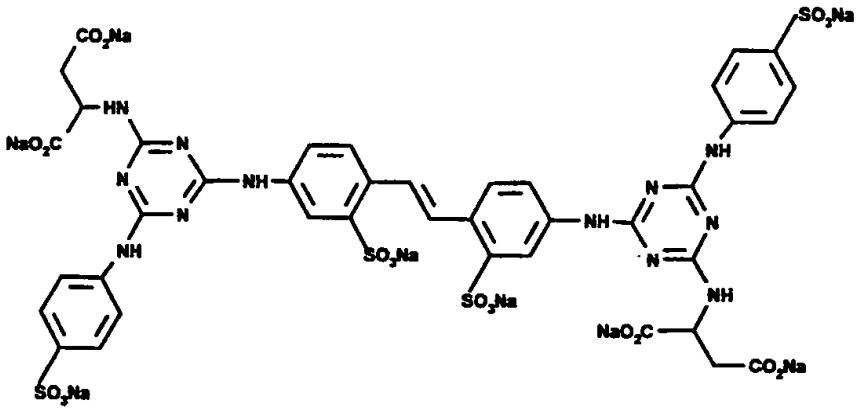
IV



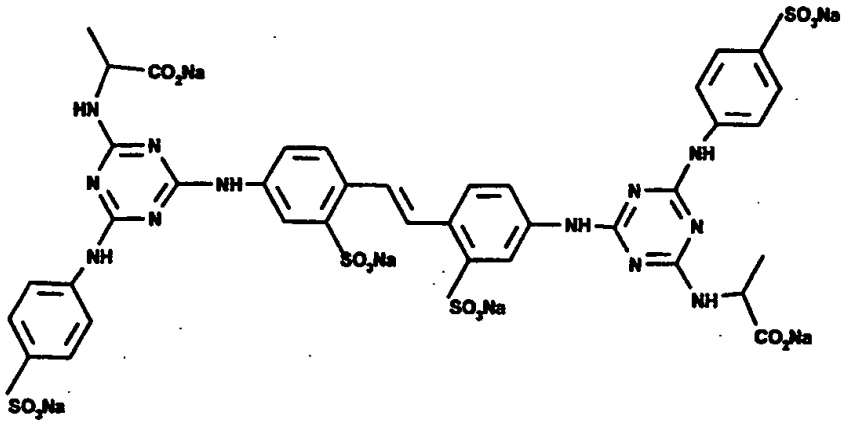
V



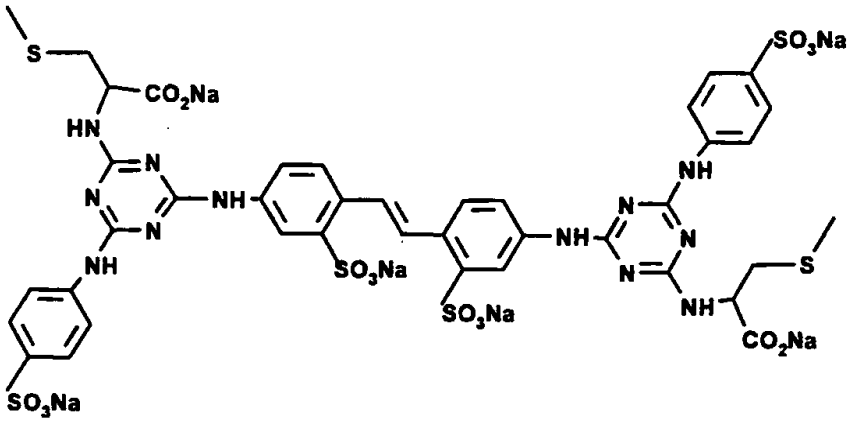
VI



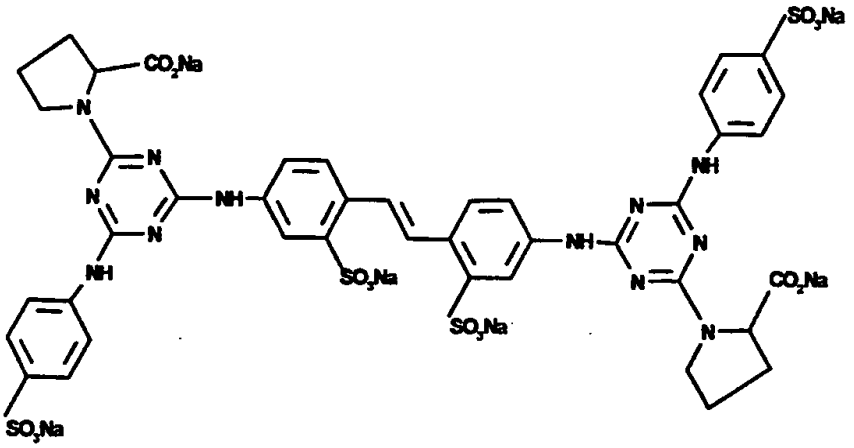
VII



IX



X



XI

The compounds according to this invention may be prepared by standard synthetic methods using readily-obtainable reagents.

The compounds may be used individually or in admixture. It has been found that some of them, particularly the aminodiacetic acid/glutamic acid - sulphanilic acid-derived material referred to hereinabove, exhibit outstanding optical brightening characteristics. The compounds according to the invention are therefore very useful as optical brightening agents (OBAs) in paper, textiles and so on.

The compounds of the invention are particularly effective when used as optical brightening agents for paper. They may be applied to paper either by addition to a paper stock prior to sheet formation or they may be incorporated into a coating composition which is subsequently applied to a paper sheet. Incorporation into a size which is then used on paper is particularly effective. The compounds may also be applied to the surface of the paper in conjunction with certain additives which are well known to boost the performance of the optical brightening agents, such as: carboxymethyl cellulose, polyethylene glycols, alkanolamines, polyvinyl alcohols etc.

The invention therefore provides a process for making paper comprising the addition of a compound of formula I to a paper stock.

Furthermore, the invention provides a process for making paper comprising the addition of a compound of formula I to a paper coating composition.

Still further the invention provides a process for treating textiles comprising the addition of a compound of formula I thereto.

The invention also provides paper comprising a compound of formula I and furthermore textiles comprising a compound of formula I.

Still further the invention provides the use of a compound of formula I as an optical brightener for detergents, paper or textiles, preferably in coating methods after paper sheet formation.

The invention is further described by reference to the following non-limiting examples, in which all parts are expressed by weight.

Preparation Example

Preparation of a compound according to Formula III.

Stage 1

A solution of 18.4 parts of cyanuric chloride in 100 parts of acetone is allowed to run into a mixture of 300 parts of crushed ice and 500 parts of water, while cooling. A solution of 20.7 parts of the sodium salt of 4,4'-diamino-2,2'stilbenedisulphonic acid in 150 parts of water is then introduced dropwise into this mixture at a temperature in the range of 0 to 5°C and the reaction mixture is kept weakly acid to Congo paper by adding sodium bicarbonate. Stirring is continued at 0 to 5°C until no primary aromatic amine group is detectable by diazotization.

Stage 2

A solution of 19.6 parts of sulphanilic acid sodium salt in 200 parts of water is added slowly to the reaction mixture from Stage 1, keeping the temperature at 5 to 10°C and the pH at neutral by simultaneous addition of dilute sodium hydroxide solution. When the addition is complete, the mixture is heated to 50°C and stirring is continued until no primary aromatic groups can be detected by diazitization.

Stage 3

15 parts of glutamic acid is added to the reaction mixture from Stage 2 and the mixture is heated to reflux. The pH is kept at 8 by addition of dilute sodium hydroxide solution during this process. The acetone is allowed to distil off and the mixture is refluxed for 5 hours. The reaction mixture is concentrated and salt is added to precipitate the product. The product is filtered off and washed with 10% brine.

Application Example 1

10 parts of the compound of formula III is dissolved in 50 parts of distilled water. 100 parts of a typical size-press starch is made up in 1000 parts of water and cooked at 90°C. It is then cooled to 60°C. The brightener solution is then incorporated into the starch solution. A paper base or board is surface coated with the starch/brightener solution in the size-press or film-press and dried at 80-120°C in the drying section of the paper machine.

A paper or board with a considerably improved degree of whiteness is thus obtained.

Application Example 2

An aqueous solution of the compound of formula III is dosed under stirring into a warm (60°C) solution of an anionic oxidised potato starch ("Perfectamyl" (trade mark) A4692), together with water to give a starch solution of 5% and a known amount of compound.

The brightened starch solution is then poured between the moving rollers of a laboratory size-press (forming a pond) and a paper base sheet (a commercial white paper 75 g/m^2, neutral sized, CIE Whiteness 72, without a size-press coating) is then passed between the rollers, through the solution. The paper coated with the wet starch solution is then dried for 5 minutes at 70°C in a flat bed drier.

The paper is weighed before application and whilst wet to determine the pick-up of wet starch solution and therefore the pick-up of starch.

Once dried, the paper sheets are allowed to condition, and the CIE Whiteness (W_{10}) of each sheet is then calculated from measurements made on a calibrated spectrophotometer.

The process is repeated with an equal amount of a commercially-available OBA ("Leucophor" (trade mark) U) substituted for the compound according to the invention.

The resulting CIE Whiteness values for the compound and the commercial product n the

paper are shown in the graph of Figure 1. The degree of Whiteness W_{10} is calculated from the formula (from ISO 105 - 502).

$$W_{10}=Y_{10}+800(0.3138-x_{10})+1700\,(0.3310-y_{10})$$

The superior performance of the compound according to the invention is noticeable from low proportions of compound

Application Example 3

An aqueous solution of a compound of formula III is dosed under stirring, into a coating composition (described below) together with water to give a constant solids content and a known amount of the compound. The brightened coating composition solution is then coated on to a suitable base paper using an automatic wire-wound bar applicator with a standard speed setting and a standard load on the bar. The paper coated with the solution is then dried in a hot air flow for 5 minutes. A known area of the paper is weighed before application and after drying to determine the coating weight applied.

Once dried, the paper sheets are allowed to condition, and the CIE Whiteness (W_{10}) of each sheet is calculated from measurements made on the same calibrated spectrophotometer.

The coating composition recipe is:

Pigment:-China Clay SPS	100 parts
Water	64.4 parts
Dispersing agent[1]	0.6 parts
Latex[2]	20 parts
20% Starch solution[3]	25 parts

Solids content approx. = 55%

1. "Polysalz" (trade mark), a sodium salt of a polyacrylic acid, is used

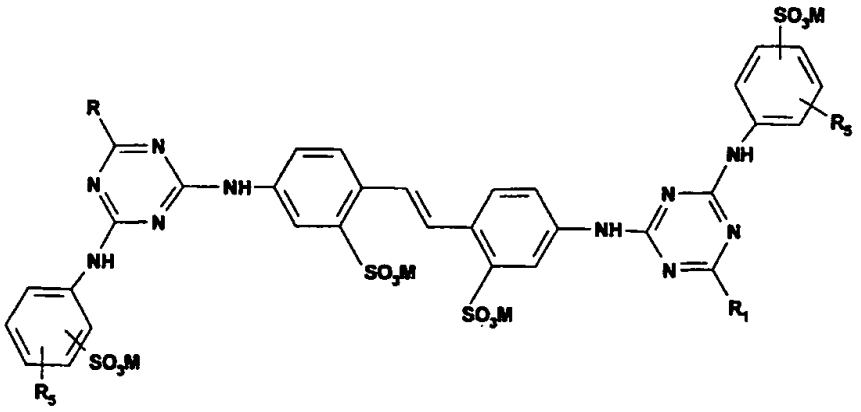
2."Acronal" (trade mark) S320D, an acrylic ester copolymer, is used

3. "Perfectamyl" A4692

The experiment is repeated using the same quantity of a commercially-available optical brightening agent. The results are shown in the graph of Figure 2. Again, it can be seen that the compound of the present invention performs significantly better than that of the commercial optical brightening agent.

Claims:

1. A compound in free acid or salt form of the formula I



I

wherein

R, R_1 are moieties which are the same or different and have the formula $-NR_2R_3$, wherein: (a) R_2 is selected from

(i) hydrogen;

(ii) C_{1-6} alkyl, optionally substituted with at least one of mercapto, C_{1-6} thioalkyl, OH and SO_3M; and

(iii) $-R_4(CO_2M)_x$

wherein R_4 is an aliphatic moiety having from 1-6 carbon atoms, those valencies not bonded with groups CO_2M being bonded with at least one of H, mercapto, C_{1-6} thioalkyl, OH and SO_3M, x is an integer of from 1 - 4 and M is selected from hydrogen, a colourless cation or an amine-derived cation;

with the proviso that, when R_2 is selected only from (i) or (ii), any group (ii) is substituted with at least both of OH and SO_3M;

(b) R_3 is selected from groups R_2, hydrogen and C_{3-6} alkyl, with

the provisos that R_2 and R_3 cannot both be hydrogen, and when one of R_2, R_3 is hydrogen, the other cannot be $-(NHCH_2CO_2H)$;

or R_2 and R_3 together with the nitrogen atom form a ring having from 5-6 members only one of which is heterocyclic, which ring is singly substituted with -COOM or $-SO_3M$;

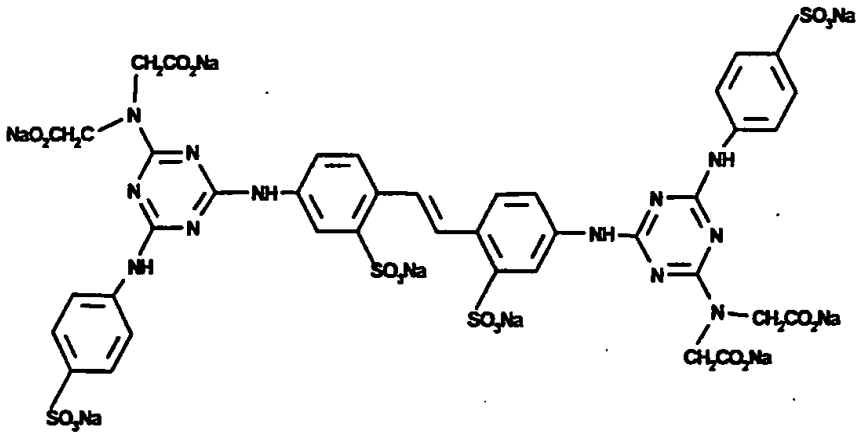
and R_5 are selected independently from the group consisting of hydrogen, methyl, C_{1-6}alkoxy and halogen.

2. A compound according to claim 1, wherein R_5 is hydrogen and the SO_3M groups on the phenylene rings attached to the triazine rings are meta or para to the connecting amino groups

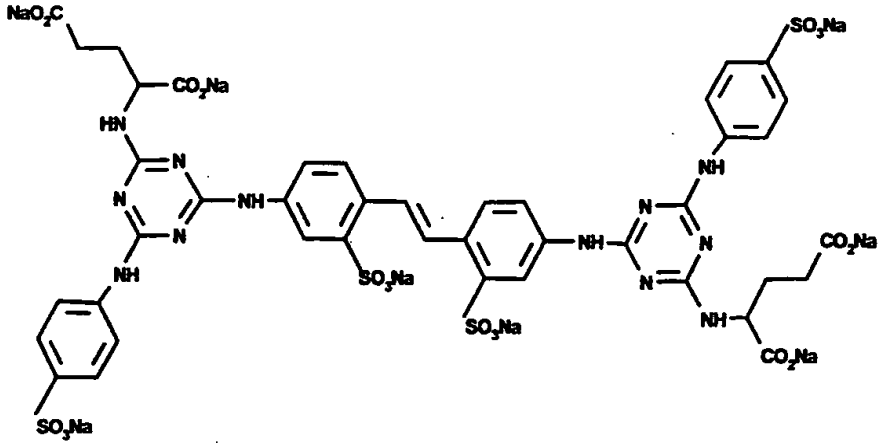
3. A compound according to claim 1, wherein R, R_1 are residues of amino-acids.

4. A compound according to claim 3, wherein the amino-acids are selected from glycine, aspartic acid, serine, hydroxyglutamic acid and alanine, and preferably glutamic acid and iminodiacetic acid.

5. A compound according to claim1, having a formulae selected from the group consisting of the formulae II and III



II



III

6. A process for making paper comprising the addition of a compound of formula I to a paper stock.

7. A process for making paper comprising the addition of a compound of formula I to a paper coating composition.

8. A process for treating textiles comprising the addition of a compound of formula I thereto.

9. Paper comprising a compound of formula I.

10. A textile comprising a compound of formula I.

11. Use of a compound of formula I as an optical brightener for detergents, paper or textiles.

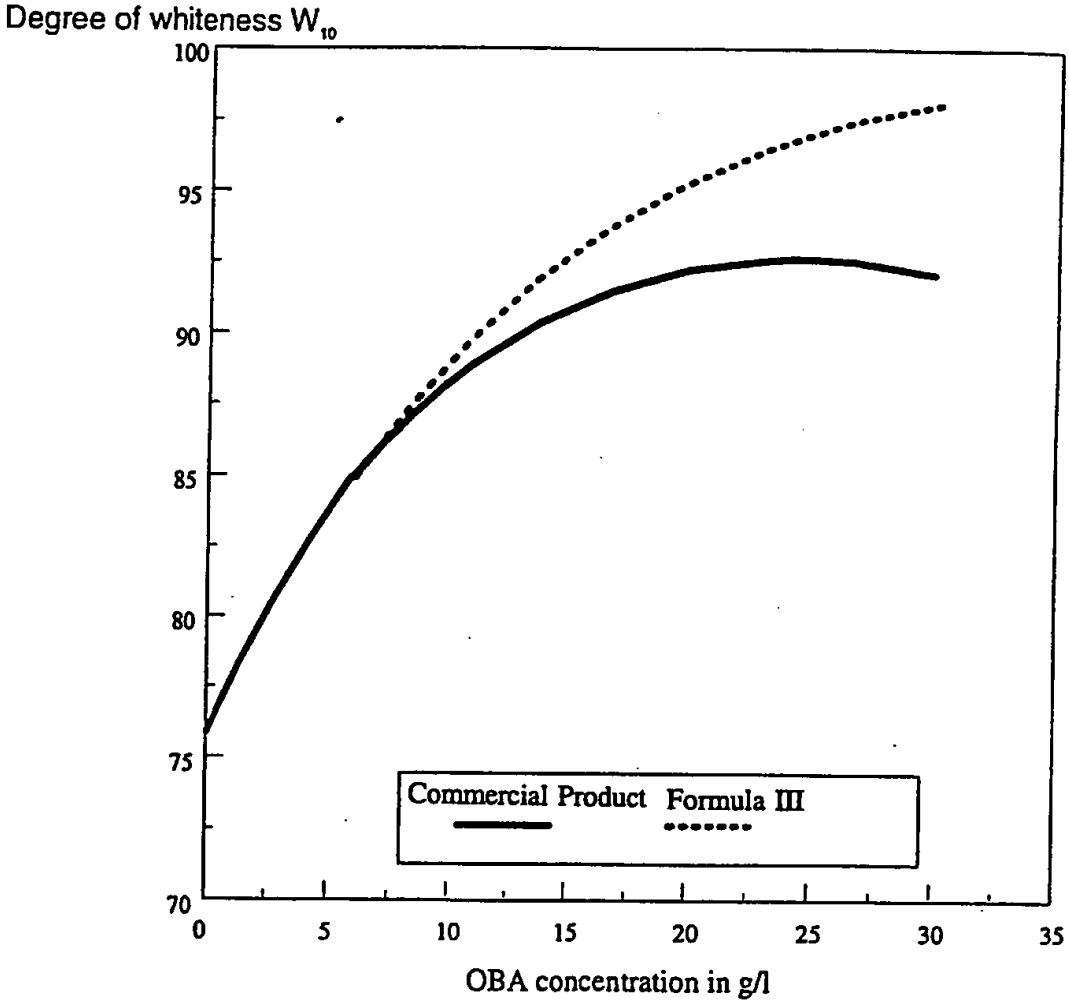

Degree of whiteness W_{10}
100
95
90
85
80
75
70
0
5
10
15
20
25
30
35
Commercial Product
Formula III
OBA concentration in g/l

Fig.1

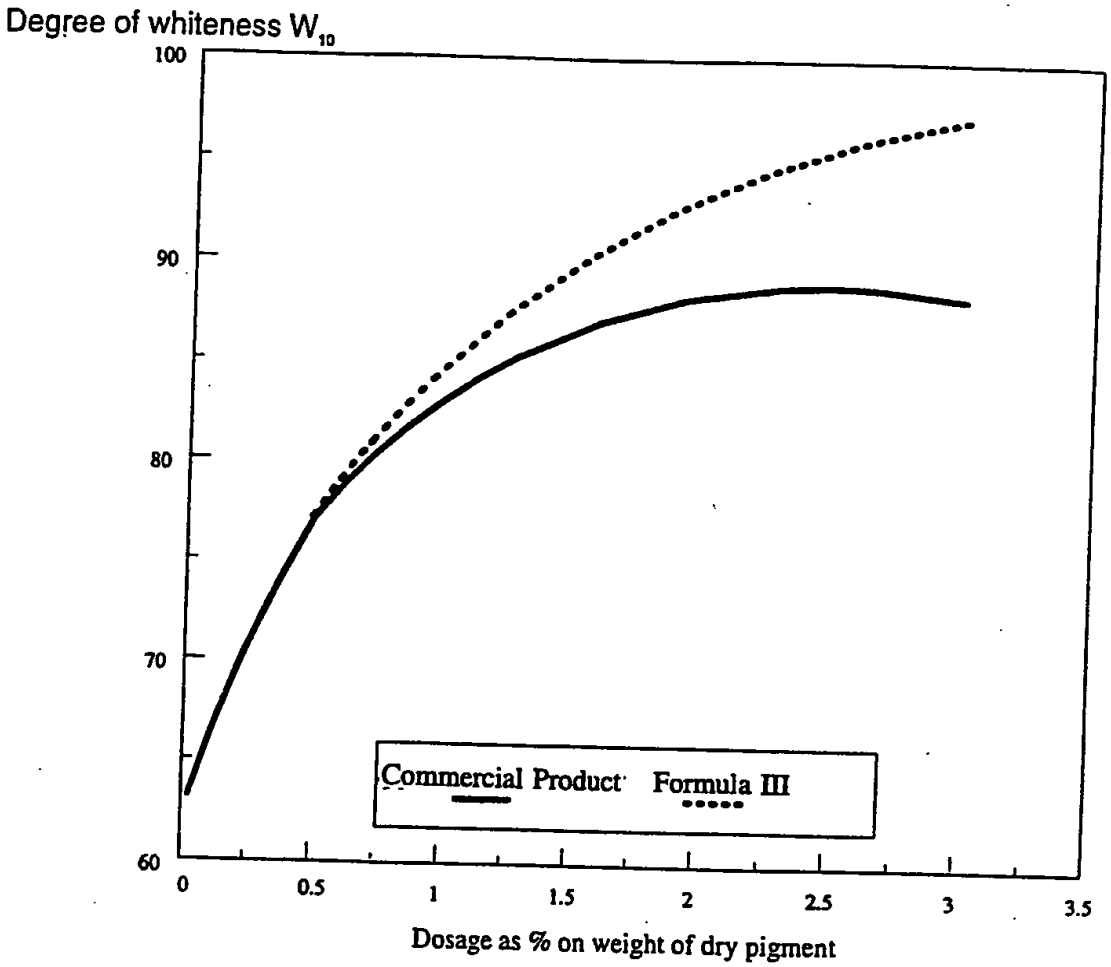

Degree of whiteness W_{10}
100
90
80
70
60
0
0.5
1
1.5
2
2.5
3
3.5
Commercial Product
Formula III
Dosage as % on weight of dry pigment

Fig.2

INTERNATIONAL SEARCH REPORT

Int. onal Application No
PCT/EP 95/02433

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D251/70 D06L3/00 C07D403/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 067 301 (J.R. GEIGY S.A.) 20 August 1971 * examples 1,3 and 17 *	1,11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
19 October 1995	25. 10. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Van Bijlen, H

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intc ional Application No
PCT/EP 95/02433

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2067301	20-08-71	BE-A-	758957	13-05-71
		DE-A-	2055996	08-06-72
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